

Adsorption and oxidation of mercury in tail-end SCR-DeNOx plants—Bench scale investigations and speciation experiments

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Abstract

The results of a bench scale investigation on mercury adsorption and oxidation under the conditions of tail-end DeNOx plants are reported. It was shown that HCl has a strong influence on mercury adsorption as well as mercury oxidation.

Adsorption of elemental mercury and HgCl₂ on a DeNOx catalyst with 2.5 wt.% V₂O₅ is appreciably in flue gases that contain HCl in concentrations below 0.5 mg/m³. Mercury adsorption increases linearly with the mercury concentration in the flue gas. The amount of HgCl₂ adsorbed on the catalysts is higher than of elemental mercury, under otherwise comparable conditions. Mercury adsorption depends on the V₂O₅ content of the DeNOx catalyst. The nature of the adsorbed mercury species was investigated by sequential chemical extraction and X-ray absorption fine structure spectroscopy. According to these methods mercury does form a Hg–O bond on the surface of the catalysts. In terms of regeneration of mercury loaded catalysts it is of interest, that more than two-third of the adsorbed mercury can be removed by washing the DeNOx catalyst at room temperature with a dilute solution containing acetic and hydrochloric acid.

In the presence of higher concentrations of HCl in the flue gas elemental mercury is no longer adsorbed but oxidized by DeNOx catalysts. The rate of oxidation decreases with increasing temperature. NO has compared to HCl only a slightly accelerating influence, whereas NH₃ shows a small detrimental effect. The simultaneous presence of NO and NH₃ inhibits the HCl assisted oxidation of elemental mercury strongly.

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1. Introduction

Mercury is a toxic trace element with extreme volatility and strong bioaccumulative properties [1]. Estimates of anthropogenic mercury emissions for Europe and North America show that combustion processes are a major contributor. There is therefore presently much interest in developing reliable methods for removing mercury from combustion flue gases.

In the high temperature region of combustion furnaces almost all mercury entering with the fuel is transformed into the elemental form (Hg^{el}). When cooling the flue gas, a series of complex reactions converts this gaseous Hg^{el} at least partially into oxidized mercury species (Hg^{ox}). In the presence of hydrogen chlorine (HCl) gas phase equilibrium conditions favour the formation of HgCl₂. However, this reaction is

generally kinetically limited [2]. HBr and Br₂ are also important flue gas constituents that facilitate the transformation of elemental Hg into oxidized species [3]. Hg^{ox} can fairly easily be removed from gases by absorptive and adsorptive means; it is therefore the preferred mercury species in flue gases.

In plant investigations showed that the widely used catalytic NOx abatement process may also have a pronounced influence on the speciation of the mercury in the flue gas [4–6]. The main objective of this process is to transform the nitrogen oxides (NO_x) into nitrogen and water by a catalytically enhanced reductive reaction with ammonia. This so called selective catalytic reduction (SCR) process is generally using titanium dioxide supported vanadium pentoxide (V₂O₅) catalysts with tungsten (WO₃) or molybdenum trioxide (MoO₃) as a promoter [7,8].

Most of the reports on mercury and SCR catalysts concentrate on the process conditions of high dust SCR plants. Here depending on the coal or waste fuel burned generally fairly high concentrations of HCl between 5 mg/

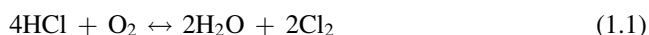
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Nm^3 and several g/Nm^3 and SO_2 up to several g/Nm^3 are encountered.

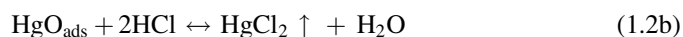
In the presence of higher HCl concentrations the mercury oxidation is of major interest. Experimental investigations have revealed that the degree of mercury oxidation across a SCR DeNOx catalyst increases with the HCl content [9,10]. Furthermore it has been shown, that SCR catalysts can produce chlorine (Cl_2) from HCl according to the Deacon reaction [11].

Chlor-Deacon:



The Cl_2 and the associated chlorine radicals (Cl^\bullet) react faster as the HCl with Hg^{el} [12]. Therefore it seems likely that the observed increased mercury oxidation by SCR catalysts in the presence of HCl might at least partly be caused by the intermediate products Cl_2 and Cl^\bullet . Another hypothesis assumes that the elemental mercury in the flue gas is adsorbed by the surface V_2O_5 and transformed into surface HgO as an intermediate which reacts fairly rapidly with HCl to form the volatile HgCl_2 :

HgO mechanism:



In most waste incineration plants and also some coal fired power plants the SCR unit is operated in the tail-end configuration. Here the flue gases have been treated upstream so that the remaining concentrations of HCl are generally well

below 10 mg/Nm^3 and the SO_2 below 100 mg/Nm^3 . Most of the remaining mercury in the flue gas at this stage is Hg^{el} , since scrubbers and active carbon adsorbers remove oxidized mercury preferentially [5,9]. The operation temperatures of tail-end SCR units are usually between 260 and 320°C . In-plant experience in waste incinerators show that under these conditions adsorption of mercury may occur [5,9]. These observations have recently been confirmed in lab-scale catalytic units [9,10].

In the present study the findings of a detailed lab scale research programme on parameters that effect mercury adsorption and oxidation under tail-end SCR-DeNOx conditions are given. The investigation focuses on:

- the concentration and temperature dependency of the adsorption equilibrium loadings of Hg^{el} and Hg^{ox} (HgCl_2) in the absence of HCl,
- the influence of co-pollutants on the equilibrium loading,
- the influence of the vanadium content of the catalyst, and
- the effect of co-pollutants on the oxidation of Hg^{el} in the presence of higher HCl concentrations.

Recently the chemical speciation of inorganic mercury on soils and fly ashes from combustion processes has been determined by sequential chemical extraction (SCE), thermal desorption and synchrotron-based X-ray absorption fine structure spectroscopy (XAFS) [13,14]. For the first time these methods have been used in the present study for speciation experiments of the mercury adsorbed on the surface of DeNOx catalysts. In this way a better understanding of the mercury adsorption, desorption and oxidation processes was aimed at.

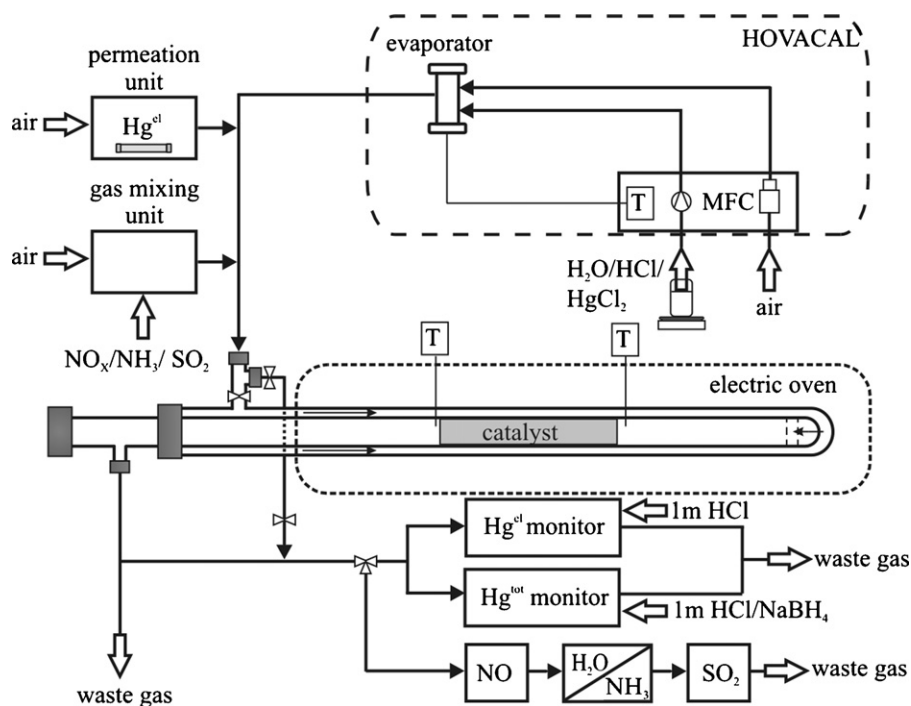


Fig. 1. Schematics of the laboratory SCR-DeNOx flow reactor.

2. Experimental

2.1. Flow reactor

For the experimental investigation a bench scale flow reactor has been operated under conditions that simulated industrial tail-end SCR-DeNOx plants. A schematic of the apparatus is given in Fig. 1.

The model flue gas of 170–240 l/h (dry, STP) was generated by mixing three different gas streams. As carrier gas, generally air metered by a mass-flow controller (MFC) was used. For some test runs SO₂, NO and NH₃ were added to the carrier gas by means of MFCs with a flow rate that the final gas contained the required pollutant concentration. With the second gas stream generated by a MFC controlled air flow the elementary mercury concentration could be introduced by means of a temperature controlled permeation tube (permeator supplied by Breittfuss Messtechnik GmbH, Germany). The third gas stream introduced the water vapour by a commercial Hovacal evaporator system (IAS Schmaeh, Germany) to the simulated flue gas. The needed quantity of water was metered by a peristaltic pump and evaporated at a temperature of 190 °C into a MFC supplied air stream so that a water content of the model flue gas of generally 15 vol.% was reached. The water mass flow introduced into the evaporator was controlled by a balance. The HCl containing gases were generated by evaporating appropriate solution of hydrochloric acid. HgCl₂ containing gases were generated in the same unit by evaporating appropriate solutions of this compound.

The mercury concentrations of about 160 µg/Nm³ applied for many experiments are by a factor of 10 higher than typically encountered in influent gases of tail-end SCR plants of waste incinerators. They were chosen according to the sensitivity of the employed continuous mercury monitors and the speciation investigation methods.

The reactor consisted of two concentric glass tubes in an electrically heated oven. The incoming simulated flue gas was heated in the outer ring cylinder to the required reaction temperature before its flow was reversed and returned in the inner cylinder of the reactor, where the DeNOx catalyst test element was placed.

The oxidation experiments were carried out on honey comb shaped catalysts with 4 × 4 channels and a length of 120 mm according to the required area velocity AV (normal gas volume per geometric surface area of the catalyst). The adsorption investigations were performed on crushed catalyst material (2 × 0.5 g). The temperature was measured by thermo elements placed up- and downstream of the catalyst material.

2.2. Catalysts

In this study commercial low-dust V₂O₅-WO₃/TiO₂ DeNOx catalysts supplied by KWH/Germany were used. The structure of the TiO₂ is of the anatase type. Table 1 summarizes characteristic data for the catalysts used in the investigation.

Table 1

Chemical and physical properties of the investigated SCR-DeNOx catalysts

	Catalyst		
	C 0	C 2.5	C 4.5
V ₂ O ₅ content (wt.%)	0	2.5	4.5
WO ₃ content (wt.%)	8.7	7.9	6.8
Pitch (mm)	4.2	4.2	4.3
Channel (mm)	3.5	3.5	3.54
Specific geometric surface area (m ² /m ³)	760	760	780
BET surface (m ² /g)	58.4	63.5	50

2.3. Chemicals

For preparing the solutions evaporated by the Hovacal system HgCl₂ with a purity of 99.5% and hydrochloric acid with 37% were obtained from Merck/Germany. A diluted solution of sodium borohydride (purity ≥96%, Merck/Germany) and sodium hydroxide (purity ≥99, Merck/Germany) was used as wet chemical reductive media to prepare the gas for the UV photometric based Hg^{tot} measurement.

2.4. Gases

Dried compressed air was purified by active carbon before being used as carrier gas.

Compressed liquefied SO₂ with a 3.8 purity, NH₃ with a 3.8 purity and compressed NO with a purity of 2.5 obtained from Messer/Germany where used to prepare the respective model flue gases.

For calibration purposes reference gases with 405 ppm SO₂ (±2%) and 900 ppm (±2%) of NO in synthetic air obtained from Messer/Germany were used during the investigation.

2.5. Mercury analysis

2.5.1. Gas phase analysis

Two continuous mercury emission monitors (Model EPM 791.907, Durag/Verewa, Germany) were used for measuring the mercury concentration in the flue gases at the inlet and outlet of the SCR reactor. Differentiating the elemental from the total mercury content of the sample gases was done by wet chemistry pulping. About 20 ml/h of a solution containing 5 g/l NaBH₄ and 20 ml/h of a 1N hydrochloric acid were introduced by peristaltic pumps into the sample gas (flow rate 80 l/h, heated to 180 °C) to reduce the oxidized mercury to elemental. Subsequently after removing the water vapour by cooling the sample gas to 4 °C and removing the SO₂ by an adsorber, filled with solid NaOH granules, the total mercury content was determined by cold vapour atomic absorption in a two absorption cell arrangement.

For the determination of the Hg^{el} the sample gas was scrubbed with 40 ml/h of a 1N HCl for removing Hg^{ox}. Then a sequence of cooler, NaOH-adsorber and cold-vapour atomic absorption photometer was used to quantify the mercury content.

The mercury analysers were calibrated with known solutions of HgCl₂ and the Hovacal evaporation unit. The detection limit

of the analysing system used was $0.5 \mu\text{g}/\text{Nm}^3$. The signal to concentration calibration curve proved to be linear up to $400 \mu\text{g}/\text{Nm}^3$.

2.5.2. Solid phase analysis

The catalyst samples were digested by aqua regia and the mercury determined by cold vapour adsorption techniques. For samples of 0.5 g the mercury detection limit was $1 \text{ mg}/\text{kg}$. The analysis was performed by the accredited laboratory of Infraleuna/Leuna, Germany.

2.6. Gas analysis for non mercury pollutants

A continuous non dispersive Binos 1001 infrared analyser (Rosemount/Germany) was used to determine the SO_2 concentration ($0\text{--}35/500 \text{ ppm}$) of the gases. NO was measured by a BINOS 1004 ($0\text{--}250/2500 \text{ ppm}$). The gas sample stream was dried in a gas cooler at 4°C before measurement in the continuous analysers.

The NH_3 and H_2O concentration of the model flue gases were checked from time to time by a continuous non-dispersive hot-gas (180°C) analyser MCS 100 (Perkin-Elmer/Sick-Maihak, Germany). Appropriate standard gases prepared by evaporation of known solutions were used to calibrate the instruments.

2.7. Sequential chemical extraction (SCE) of mercury-loaded DeNOx catalysts

In order to determine the bonding of the adsorbed mercury extraction experiments have been conducted according to the procedure recommended by Bloom et al. [13].

Catalyst samples ($2.5 \text{ wt.}\% \text{ V}_2\text{O}_5$) loaded at 290°C either with $2000 \mu\text{g}/\text{Nm}^3 \text{ Hg}^{\text{el}}$ or Hg^{ox} (HgCl_2) containing gas ($15 \text{ vol.}\% \text{ H}_2\text{O}$) were successively washed with five different extraction solvents in sequence: F1—deionised water, F2—

$0.1 \text{ M CH}_3\text{COOH} + 0.01 \text{ M HCl}$, F3— 1 M KOH , F4— 12 M HNO_3 , F5—aqua regia. Extractions were performed using a $100:1$ liquid-to-solid-ratio. Each extraction step was conducted for $18 \pm 3 \text{ h}$ with constant agitation at room temperature. At the end of each step the samples were centrifuged and then the supernatant liquid was filtered through a $0.45 \mu\text{m}$ Teflon filter. The solid was re-suspended in the same extractant, re-centrifuged and re-filtered. The two combined liquids were filled to 100 ml and analysed by Infraleuna/Leuna, Germany.

Results of two extraction experiments have been evaluated, whereby the extraction steps were conducted on crushed catalyst material as well on milled catalyst pieces.

2.8. XAFS investigations

XAFS experiments were performed at the HASYLAB (DESY/Hamburg) on the beam line A1 with regular beam line configuration (Si (1,1,1) monochromator, three ionization chambers). An Au foil was used for the calibration of the monochromator (zero-point of energy at $11,990 \text{ eV}$) and an aluminium filter to enhance the signal/noise ratio.

The catalyst samples were prepared by exposing them to Hg^{el} or Hg^{ox} (HgCl_2) containing model gases ($1.5\text{--}2 \text{ mg Hg}/\text{Nm}^3$, $15 \text{ vol.}\% \text{ H}_2\text{O}$, 170 and 290°C). Small amounts of these samples as well as pure mercury compounds were mixed with cellulose and pressed into 13 mm pellets. XAFS investigations were conducted on these pellets at the mercury L_{III} edge at $12,284 \text{ eV}$. All measurements on the catalysts samples were carried out in the fluorescence mode using a 5-pixel Ge-detector.

Analysis of the spectral data using the IFFEFIT fitting program Athena consisted in dividing the XAFS spectrum into separate X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions. The XANES region was analysed by smoothing and differentiating the spectrum. As has been noted previously [14,15] and also

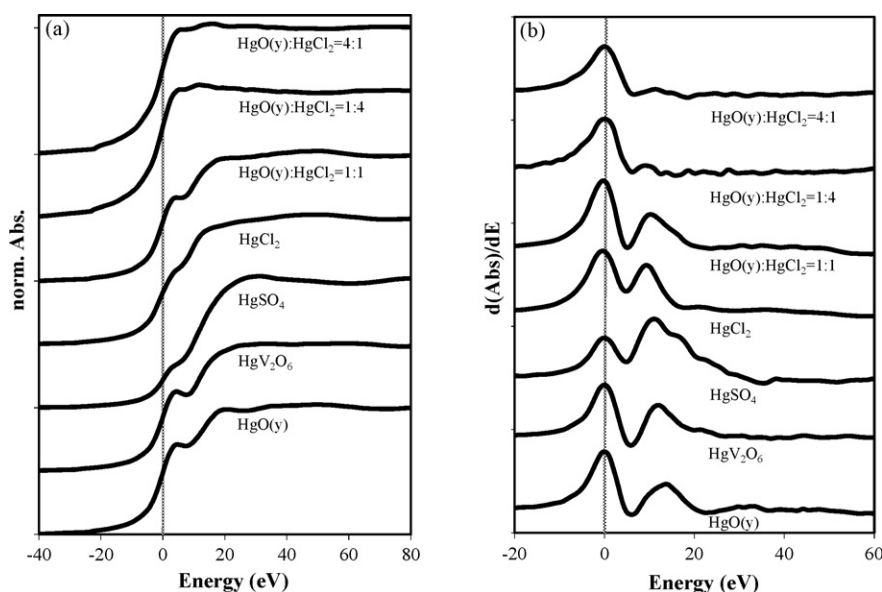


Fig. 2. Mercury L_{III} XANES and first derivative spectra of selected mercury compounds (zero point of energy corresponds to $12,284 \text{ eV}$).

found in own measurements (Fig. 2a) there are two typical inflection points on the mercury absorption edge. These inflection points give rise to two distinct peaks in the differentiated dAbs/dE spectrum of mercury compounds (Fig. 2b), owing to transitions to orbitals mainly 6s and 6p in character [16]. The spacing and relative intensities (peak height ratio H_R) of these two peaks – taken from the first derivative spectrum – reflect the chemical bonding of the nearest neighbor (NN) coordination sphere around the mercury ion [14]. The distance of these inflection points (IPD = inflection point difference) generally correlates with the differences in the ionic character of the Hg–NN bond: As shown in Table 2 the more ionic mercury compounds such as HgO (where the Hg atom is surrounded by relatively small oxygen anions) have large IPD values, whereas more covalent bonding results in smaller IPD values [14,17]. Huggins et al. [14] proposed to use the peak height ratio H_R of the two peaks as a parameter that reflects the fraction of elemental mercury involved in the adsorption process, because Hg^{el} exhibits a single peak only.

Analysing the EXAFS region consisted in fitting the data to obtain the chi spectrum, converting this from real space to the k -space and applying a Fourier transform to the k^3 -weighted chi vs. wave vector spectrum. The resulting radial structure function (RSF) represents the local structure around the absorbing mercury atom resp. the bond distance between the mercury atom and its nearest neighbor. This RSF peak position of various mercury compounds correlates inversely with the IPD value from the XANES spectrum (Table 2).

3. Results and discussion

Generally under high dust conditions mercury adsorption by the SCR-DeNOx catalysts is negligible. In terms of pollution control here the oxidation and reduction of mercury species are of paramount interest. The situation may be different in tail-end SCR plants. Here, depending on the efficiency of the up-stream flue gas treatment systems, the flue gases may contain HCl concentrations well below 1 mg/Nm³. In these low hydrogen halide gases mercury adsorption plays a dominant role [5,9]. In the first series of experiments parameters that affect the amount of mercury to be adsorbed under the worst case condition of a

HCl free gas were studied. Whereas adsorption of mercury on DeNOx catalysts might be regarded as beneficial in terms of environmental effects the uncontrolled desorption of the adsorbed mercury has to be avoided, in order to meet mercury emissions limits, which are continuously monitored. Consequently we conducted some experiments with regard to these aspects as well.

Hg^{el} entering the tail-end SCR plant might be oxidized. Mercury leaving the stack with the flue gas plume as oxidized, water soluble species is likely to be wet deposited and therefore contributing to local or hot spot mercury deposition in the vicinity of the mercury emitter. Hg^{el} with an average half live of 1 year on the other hand will contribute to the global ambient mercury concentration. Therefore not only the total mercury content but also the speciation of the mercury being emitted is of interest. Mercury entering a tail-end SCR plant will be dominantly Hg^{el} . The question is whether under typical tail-end conditions this speciation will be changed. We conducted oxidation experiments under relevant conditions in order to give an answer also to this question.

3.1. Mercury adsorption on SCR-DeNOx catalysts

The focus was placed on mercury adsorption on DeNOx catalysts under equilibrium conditions. The catalyst sample was exposed for several days to the gas stream until the mercury contents of the gas phase at the inlet and the outlet was the same. Then the experiment was carried on for at least two additional days to make sure that the equilibrium loading of the catalysts was reached. As standard conditions a temperature of 290 °C and carrier gas with a mercury concentration of 160 µg/Nm³_{dry} as elemental mercury or HgCl₂ and 15 vol.% H₂O in air were chosen. As standard the catalysts C 2.5 of Table 1 with 2.5 wt.% V₂O₅ was used.

3.1.1. Effect of co-pollutants on mercury adsorption on SCR-DeNOx catalysts

An average mercury equilibrium loading of 151 mg/kg on the standard catalysts under standard condition was measured. Considering the high adsorption temperature of 290 °C this value has to be regarded as high in comparison to the average abundance of 0.08 mg/kg of mercury in the earth crust [18].

In Table 3 it is shown how this equilibrium adsorption loading is influenced by co-pollutants in the gas. Water and 400 ppm of NO have only a small effect within the variance of the determination. 400 ppm NH₃ lower the adsorption slightly whereas 70 ppm of SO₂ cause an increase.

Among the gas constituents typical for tail-end DeNOx plants the dominant effect on the mercury adsorption is exercised by the HCl concentration. The presence of 3 ppm HCl reduces the adsorption of the mercury on the model catalyst by almost two orders of a magnitude. From these data we learn that the efficiency of the HCl removal equipment upstream of the DeNOx plant is of paramount importance for the quantity of mercury that will be adsorbed, if mercury enters the DeNOx catalyst.

Table 2
Characteristic XAFS data for mercury compounds (RSF data are phase-shift uncorrected)

Mercury compound	IPD (eV)	RSF (Å)
HgO (red)	13.3/12.8 ^a	1.65/1.68 ^a
HgO (yellow)	13.6/13.3 ^a /13.6 ^b	1.64
HgV ₂ O ₆	12	1.74
HgSO ₄	10.9/9.5 ^a	1.86
HgCl ₂	9.2/8.4 ^a /8.8 ^b	1.87/1.92 ^a
HgO (yellow):HgCl ₂ = 1:1	10.3	1.78
HgO (yellow):HgCl ₂ = 1:4	9.1	1.74
HgO (yellow):HgCl ₂ = 4:1	11.3	1.67
Hg ^{el} (liquid)	0 ^a	

Own measurements and data ^ataken from Huggins et al. [14], ^btaken from Riddle et al. [17].

Table 3

Influence of co-pollutants on the adsorption of Hg^{el} on a SCR catalyst at 290 °C

	Co-pollutant					
	Dry	15 vol.% H_2O	400 ppm NO	400 ppm NH_3	70 ppm SO_2	3 ppm HCl
Hg loading (mg/kg)	161 ± 10	151 ± 2	180 ± 3.5	142 ± 33	250 ± 7	3.5 ± 0.2

Remarks on experimental conditions: catalyst: 1 g C 2.5, crushed material; gas composition: air, 15 vol.% H_2O , $160 \mu\text{g}/\text{Nm}^3 \text{Hg}^{\text{el}}$; gas flow: 170 l/h.

3.1.2. Mercury loading of a SCR-DeNOx catalyst as a function of the gas phase mercury concentration

In subsequent investigations the mercury adsorption under worst case conditions – the absence of HCl – has been studied in order to obtain data on the maximum mercury content to be expected in tail-end DeNOx catalysts. A wide range of mercury gas phase concentrations between 10 and $1700 \mu\text{g}/\text{Nm}^3$ has been covered in order to elucidate somewhat the adsorption mechanism underlying this high temperature adsorption process. Fig. 3 depicts the adsorption isotherm of Hg^{el} on the standard catalyst for temperatures of 260, 290 and 320 °C.

As expected the adsorption loading decreases with increasing temperature. Within the experimental uncertainty the adsorption loading of the catalyst appears to be a linear function of the gas phase Hg^{el} concentration.

Mercury loadings up to 2500 mg/kg are observed. A BET surface of $50 \text{ m}^2/\text{g}$ is typical for DeNOx catalysts. One atom Hg^{el} is quoted to have a radius of 151 pm [18]. From this radius an adsorption surface area of 0.0912 nm^2 and a mercury loading value of 183 g/kg catalysts is calculated for a monomolecular surface loading. The values in Fig. 3 reach about 1% of this theoretical monomolecular surface coverage.

The mercury loading of the standard catalyst has been studied also in the presence of HgCl_2 containing gases. The resulting isotherms are also to be described as linear functions of the gas phase concentration or vapour pressure. In Table 4 the resulting linear function of the HgCl_2 adsorption isotherms are compared with the results from the Hg^{el} adsorption experiments. The mercury loading of the catalyst is higher in the presence of HgCl_2 as compared to Hg^{el} . The temperature

dependence of the adsorption process is different as well. From the temperature dependence of the adsorption isotherms the nominal isosteric heat of adsorption for Hg^{el} was calculated as 61 kJ/mol whereas the equivalent value for the HgCl_2 adsorption was 17 kJ/mol. These values have to be compared with an enthalpy of evaporation of 59.1 kJ/mol for liquid mercury [18].

From an engineering point of view the higher adsorption heat for Hg^{el} means that compared to HgCl_2 the adsorption of Hg^{el} will gain more importance with decreasing temperature. The low surface adsorption energies for HgCl_2 could be the result of physical forces being mainly responsible for the adsorption on the surface of the DeNOx catalyst. In the case of elemental mercury the higher adsorption energy could be an indication of some form of chemisorption. The linear trend of the adsorption isotherm indicates to a Langmuir type of adsorption process for low partial pressure and low surface coverage. These results show that a linear extrapolation from the relatively high Hg concentration chosen for the experiments to lower concentrations seems to be a reasonable approach.

3.1.3. Effect of the V_2O_5 content of the catalyst on mercury adsorption

SCR-DeNOx catalysts for tail-end application contain TiO_2 as porous carrier, WO_3 and in some cases MoO_3 as promoter and V_2O_5 as DeNOx active compound. In terms of mercury adsorption each of these ingredients might be the active centre. In order to clarify somewhat the influence of the composition of the catalyst on the adsorption the three catalysts listed in Table 1 have been selected. Their main difference is in the V_2O_5 content, which varied from 0 to 4.5 wt. %.

The equilibrium adsorption loadings of these catalysts in a gas containing $160 \mu\text{g}/\text{Nm}^3$ mercury as Hg^{el} or HgCl_2 have been determined for standard conditions. The results are listed in Table 5. The HgCl_2 adsorption is for all catalyst higher than for Hg^{el} . In the absence of V_2O_5 almost no Hg^{el} is adsorbed and HgCl_2 is considerably reduced. V_2O_5 contents from 2.5 to 4.5 wt. % do not cause a further increase of the adsorption of oxidized mercury, whereas there is still an increase in the adsorption of Hg^{el} to be observed.

The experiments show the importance of V_2O_5 for the mercury adsorption in general. Judging from the mercury loadings in Table 5 it seems that the sites for the adsorption of Hg^{el} and HgCl_2 differ somewhat.

3.1.4. Speciation of the mercury adsorbed on SCR-DeNOx catalysts

3.1.4.1. Sequential chemical extraction and thermal desorption. The obtained averaged results of the mercury removed

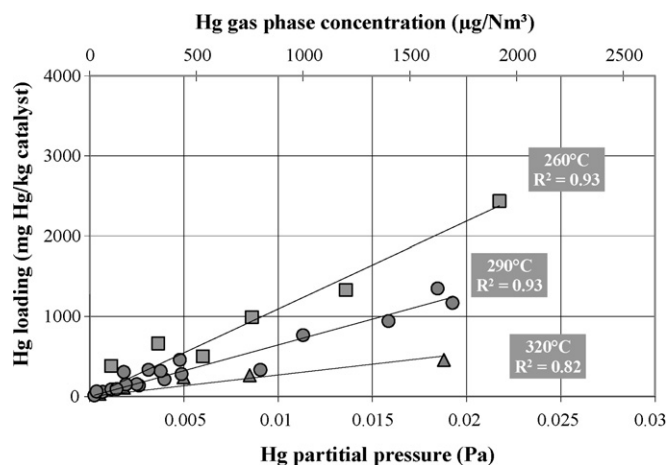


Fig. 3. Hg^{el} adsorption isotherms of a SCR catalyst. Remarks on experimental conditions: catalyst: 1 g C 2.5, crushed material; gas composition: air, 15 vol.% H_2O , 10–1700 $\mu\text{g}/\text{Nm}^3 \text{Hg}^{\text{el}}$; gas flow: 170 l/h.

Table 4
Adsorption isotherms of Hg^{el} and HgCl_2 of a SCR catalyst

	Hg^{el}	Hg^{ox} (HgCl_2)
Temperature ($^{\circ}\text{C}$)		
260	$X \text{ (mg/kg)} = 109368P \text{ (Pa)}, R^2 = 0.93$	$X \text{ (mg/kg)} = 141337P \text{ (Pa)}, R^2 = 0.92$
290	$X \text{ (mg/kg)} = 64476P \text{ (Pa)}, R^2 = 0.93$	$X \text{ (mg/kg)} = 131802P \text{ (Pa)}, R^2 = 0.64$
320	$X \text{ (mg/kg)} = 26941P \text{ (Pa)}, R^2 = 0.82$	$X \text{ (mg/kg)} = 96193P \text{ (Pa)}, R^2 = 0.93$
Isosteric adsorption heat (kJ/mol)	61	17

Remarks on experimental conditions: catalyst: 1 g C 2.5, crushed material; gas composition: air, 15 vol.% H_2O , 10–1700 $\mu\text{g}/\text{Nm}^3$ $\text{Hg}^{\text{el}}/\text{HgCl}_2$; gas flow: 170 l/h.

Table 5
Influence of the V_2O_5 content of the SCR catalyst on the adsorption of Hg^{el} and HgCl_2 at 290 $^{\circ}\text{C}$

	Catalyst		
	C 0	C 2.5	C 4.5
V_2O_5 content (wt.%)	0	2.5	4.5
Hg loading by Hg^{el} impact (mg/kg)	0.3 ± 0.47	151 ± 2	289 ± 1.4
Hg loading by Hg^{ox} (HgCl_2) impact (mg/kg)	357 ± 7	1160 ± 46.7	1019 ± 158.4

Remarks on experimental conditions: catalyst: 1 g C 0, C 2.5 and C 4.5, crushed material; gas composition: air, 15 vol.% H_2O , 160 $\mu\text{g}/\text{Nm}^3$ Hg^{el} ; gas flow: 170 l/h.

from the catalyst samples in each sequential chemical extraction step are given in Fig. 4. The results of the two repeated determinations proved to be fairly reproducible. For example the percentage of the total mercury removed by the F2 extraction solution varied in the two repeated experiments by $\pm 10\%$ from the average for Hg^{el} and by $\pm 7\%$ for HgCl_2 loaded catalysts. In the case of the Hg^{el} samples the mercury extracted by the solutions F1 to F5 accounted for 75% and in the case of the HgCl_2 samples for 82% of the total mercury.

The extraction patterns for the Hg^{el} and HgCl_2 loaded catalyst samples are similar. This astonishing result indicates that the speciation of the mercury on the surface of the catalysts is similar. According to [13] the mercury extracted by the F2 solution contains only a small quantity of HgCl_2 . Two third are caused by HgO or HgSO_4 . HgO could be the result of a reaction between the V_2O_5 on the surface of the catalysts and mercury. Although mercury was adsorbed from a gas containing no SO_2 the

occurrence of HgSO_4 cannot be excluded since DeNOx catalysts contain from their production process generally 1–2% sulphate.

In order to get some additional information on the speciation of the mercury on the surface of the catalysts some preliminary thermal desorption experiments have been conducted. For this sample loaded with about 1000 $\mu\text{g}/\text{Nm}^3$ mercury as Hg^{el} or HgCl_2 at standard conditions at 290 $^{\circ}\text{C}$ where subsequently treated for 24 h at 290, 300 and 350 $^{\circ}\text{C}$ in a mercury free air stream. During these experiments the mercury content of the catalysts decreased from 770 to 26 mg/kg for Hg^{el} respectively from 2010 to 62 mg/kg for HgCl_2 loaded catalyst. In both cases even at 350 $^{\circ}\text{C}$ about 3% of the adsorbed mercury remained adsorbed.

3.1.4.2. XAFS investigations. The mercury contents of the catalyst samples examined in the XAFS experiments varied between 0.8 and 5.3 g/kg. Consequently 9–22 XAFS scans per sample were performed to obtain analysable spectra. Even at this high number of scans the majority of samples did not provide sufficient strong EXAFS signal to gain meaningful radial structure functions (RSFs) because of the poor signal/noise ratio.

XANES spectra for six samples are shown in Fig. 5a. The resulting derived spectral data are given in Fig. 5b. The corresponding IPD values are listed in Table 6. The IPD values for the catalyst samples are in the excess of 10 eV. There are no marked differences between the spectra from Hg^{el} and HgCl_2 catalysts samples. These high IPD values are characteristic of Hg–O bonds [14]. In this respect the results from the sequential selective extraction experiments are confirmed.

The distinct second peak in the dAbs/dE spectrum (Fig. 5b) and the high IPD values suggest that there are no appreciable amounts of elemental mercury on the surface of the sample catalyst even in gases that contained solely Hg^{el} . The adsorption of Hg^{el} must involve some sort of chemisorption resulting in Hg–O bonds.

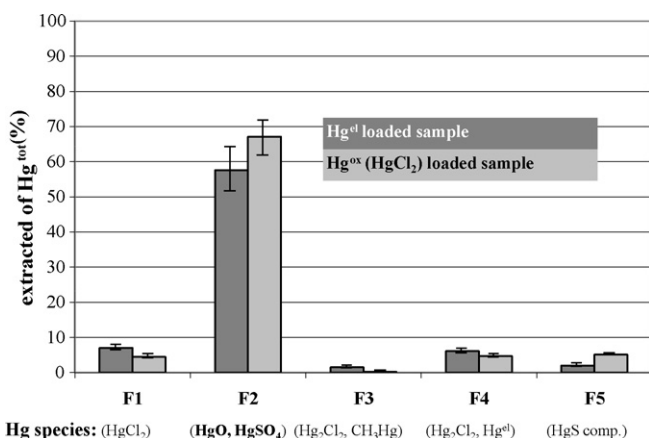


Fig. 4. Sequential chemical extraction of Hg^{el} and Hg^{ox} (HgCl_2) adsorbed on a SCR catalyst at 290 $^{\circ}\text{C}$, averaged results of two measurements. Remarks on loading conditions: catalyst: 1 g C 2.5, crushed material; gas composition: air, 15 vol.% H_2O , 2000 $\mu\text{g}/\text{Nm}^3$ $\text{Hg}^{\text{el}}/\text{HgCl}_2$; gas flow: 170 l/h.

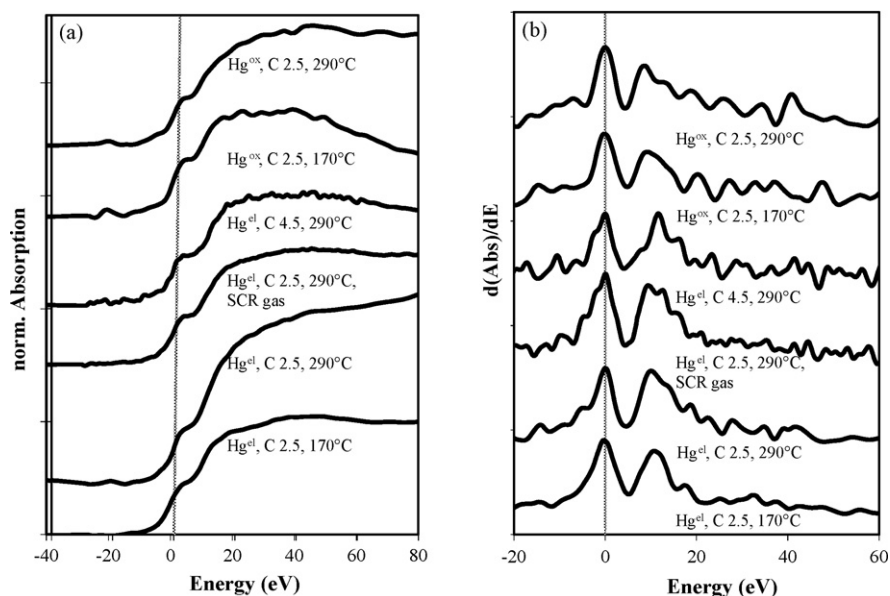


Fig. 5. Mercury L_{III} XANES and first derivative spectra of different mercury loaded catalyst samples (Zero point of energy corresponds to 12,284 eV). Remarks on loading conditions: see Table 6.

3.2. Mercury desorption from SCR-DeNOx catalysts

From the experiments discussed so far it is obvious that DeNOx catalyst may adsorb considerable quantities of mercury from flue gases that contain only small HCl concentrations. The standard catalyst C 2.5 of this investigation for example will adsorb at 290 °C in a HCl free flue gas with 10 µg/Nm³ mercury in the form of Hg^{el} about 7.3 mg mercury per kg of catalyst.

This mercury on the surface of the catalysts can easily be volatilized by HCl. In experiments it was shown that 1–50 mg/m³ HCl will volatilize the adsorbed mercury in relatively short time resulting in mercury concentration episodes of several hundred of µg/Nm³ in the flue gas downstream of the DeNOx catalyst. A continuous mercury analyser operated in such a flue gas behind a SCR plant will record such episodes which are likely to violate the legal maximum concentration set for mercury emissions.

Tail-end DeNOx plants operating on flue gases that contain small HCl concentration will adsorb mercury which was not removed in the upstream flue gas cleaning steps. The mercury content of the catalysts operating under such conditions should

be regularly examined. If higher mercury loadings accumulate one should remove it in a controlled manner so that it is not released to the atmosphere with the flue gases causing mercury episodes. One way of doing this would be washing the catalysts with an acetic and hydrochloric acid containing solution similar to the extraction solution F2 in the experiments discussed in Section 3.1.4. In this way up to 80% of the mercury adsorbed on the standard catalysts C 2.5 could be removed, see Fig. 3. During this extraction step about 10% of the vanadium is removed as well. This loss has to be replenished in a subsequent step by soaking with a vanadium containing solution. Washing of DeNOx catalysts is an industrially established process for activity regeneration purposes [19]. This service is offered commercially by several specialised companies.

3.3. Mercury oxidation by SCR-DeNOx catalyst under tail-end flue gas conditions

The results in Table 3 indicate that Hg^{el} will not be appreciably adsorbed by DeNOx catalysts in flue gases with HCl in the mg/m³ (1 ppm–1.6 mg/m³) concentration range. The mercury entering a tail-end DeNOx plant will be predominantly in the elemental form. An interesting question is whether the Hg^{el} will be oxidized when passing through the DeNOx plant in the presence of HCl. Hg^{ox} formed in this way and released to the atmosphere with the stack gas is more likely to be deposited in the local vicinity of the emission source by wet and dry deposition than Hg^{el}, which is more globally distributed with an average atmospheric lifetime of 1 year.

In Table 7 the experimental results of an investigation on the oxidation of Hg^{el} under DeNOx tail-end conditions are summarized. Co-pollutants affect the oxidation rate considerably. While in air almost no oxidation can be observed, 400 ppm NO has already a small positive effect on the oxidation. Experiments not listed showed, that SO₂ has only a marginal and

Table 6
Characteristic XAFS data for various mercury loaded catalyst samples (RSF data are peak-shift uncorrected)

Sample	Hg content (mg/kg)	IPD (eV)	RSF (Å)
Hg ^{el} , C 2.5, 170 °C	5020–5320	10.4	1.83
Hg ^{el} , C 2.5, 290 °C	1640–3361	10.2	
Hg ^{el} , C 2.5, 290 °C + SCR gas	4541	9.6	
Hg ^{el} , C 4.5, 290 °C	1690	11.3	
Hg ^{ox} (HgCl ₂), C 2.5, 170 °C	1410	10.1	
Hg ^{ox} (HgCl ₂), C 2.5, 290 °C	791–1492	9.7	

Remarks loading conditions: catalyst: 1 g C 2.5 and C 4.5, crushed material; gas composition: air, 15 vol.% H₂O, 1500–2000 µg/Nm³ Hg^{el}/HgCl₂, SCR gas: add. 70 ppm SO₂, 400 ppm NO, 300 ppm NH₃, 0.3 ppm HCl; gas flow: 170 l/h.

Table 7

Influence of co-pollutants on the oxidation of Hg^{el} in the presence of a SCR catalyst

Temperature (°C)	Co-pollutant			
	400 ppm NO	0.3 ppm HCl	3 ppm HCl	0.3 ppm HCl, 400 ppm NO, 300 ppm NH_3 , 70 ppm SO_2
Hg^{ox} after catalyst (%)				
260	10	97	97	43
290	7	89	100	10
320	6	72	100	8

Remarks on experimental conditions: catalyst: C 2.5, monolith (4×4 channels, length of 120 mm), AV 10 m/h; gas composition: air, 15 vol.% H_2O , 160 $\mu\text{g}/\text{Nm}^3$ Hg^{el} + co-pollutants; gas flow: 240 l/h.

that NH_3 has a negative effect on the mercury oxidation. These findings have also been observed elsewhere [9,10]. The strongest effect on the Hg^{el} oxidation likely to be encountered in tail-end flue gases is exercised by HCl. Concentration as small as 0.5 mg/ Nm^3 (~ 0.3 ppm) HCl will already cause a degree of oxidation of higher 90% under the investigated conditions. From the data in Table 7 it can be seen, that the HCl induced oxidation of Hg^{el} has a for chemical reactions unusual negative temperature dependence. This effect might be caused by an adsorption step forming a reactive species for the Hg^{el} oxidation that is rate determining for the overall reaction.

The positive effect of the HCl is counteracted by the DeNOx reaction as can be seen from the experimental results given in the last column of Table 7. The oxidation rates for a flue gas with 0.5 mg/ Nm^3 HCl (~ 0.3 ppm), 70 ppm SO_2 , 400 ppm NO and 300 ppm NH_3 are given. Under the chosen experimental conditions the oxidation rate of the mercury is reduced below 50%. The negative effect of the temperature on the overall oxidation rate is again to be observed. From these results it seems that an operating tail-end DeNOx plant will oxidize only partially the flue gases entering Hg^{el} .

Experiments recently conducted with more sensitive mercury monitors at Hg concentrations as low as 3 $\mu\text{g}/\text{Nm}^3$ (prepared for publication) showed that oxidation is following a first order kinetics. Therefore working at higher concentrations as done within this study should give results also valid for a lower concentration range.

4. Conclusions

The adsorption isotherms of this investigation give quantitative information on the mercury adsorption potential of DeNOx catalysts for elemental mercury and HgCl_2 . From these investigations one can conclude that mercury can be appreciably accumulated in tail-end DeNOx catalysts. Concentrations of 10–20 $\mu\text{g}/\text{Nm}^3$ are often met in such plants operated in waste incineration plants, so that assuming a concentration of 15 $\mu\text{g}/\text{Nm}^3$ up to 19 mg/kg of mercury can be adsorbed on the investigated catalysts at 260 °C under equilibrium conditions and in absence of HCl. This Hg loading represents a worst case scenario.

In general mercury adsorption:

- decreases with increasing temperature,
- increases about linearly with the mercury concentration in the flue gas,

- depends on the speciation of the mercury in the flue gases and increases from elemental to oxidized mercury,
- is strongly inhibited by HCl; a concentration of 3 ppm HCl reduces for example the mercury adsorption by two orders of magnitude under the investigated conditions,
- is only slightly decreased by NH_3 and slightly increased by SO_2 ,
- is dependent on the V_2O_5 content of the DeNOx catalyst,
- involves chemisorption and formation of Hg–O bondings on the catalyst surface.

The strong dependence of the mercury adsorbance on the HCl contents might cause mercury episodes in the flue gas down-stream of a DeNOx plant, with mercury concentrations being orders of magnitudes higher than up-stream.

The adsorbed mercury can be removed to more than two-third by washing the catalyst with a diluted solution of acetic and hydrochloric acid. This might provide a mercury sink of technical importance.

In the presence of HCl the Hg^{el} is oxidized by the DeNOx catalyst. This oxidation decreases with increasing temperature. NO has compared to HCl only a small accelerating influence on the mercury oxidation, whereas NH_3 has a small detrimental effect. The simultaneous presence of NO and NH_3 in the flue gas entering the DeNOx catalyst inhibits strongly the HCl assisted oxidation of the Hg^{el} . The effect might be associated with intermediates produced by the DeNOx reaction on the surface of the catalyst under these process conditions. The mechanistic and modelling work on mercury oxidation will have to take this strong effect into account in the future.

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